

**CORRELATION BETWEEN THERMAL DESORPTION
SPECTROSCOPY AND OPTICAL SECOND HARMONIC GENERATION
FOR MONITORING SURFACE COVERAGES**

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Optical second harmonic generation was used to monitor CO coverages on Cu(100) and Ni(111) in an ultrahigh vacuum chamber. In both cases, the adsorption kinetics were found to obey the simple Langmuir model. In monitoring CO coverages remained on Cu(100) and Ni(111) during a thermal desorption process, optical second harmonic generation correlates well with thermal desorption spectroscopy.

Optical second harmonic generation (SHG) has recently been found to be an effective probe for surface studies [1,2]. As a tool for monitoring molecular adsorption and desorption at a surface or interface, it has a sensitivity capable of detecting a submonolayer of adsorbates and can be used for in situ measurements with a very fast time response [4]. Being an optical method, it is applicable to all interfaces accessible by light including those between condensed media.

The possibility of using SHG to monitor quantitatively the amount of adsorbates on a surface with a good time resolution is most interesting for many surface studies. Calibration is however often a problem. For samples studied in an ultrahigh vacuum (UHV) chamber, surface coverages that exhibit clear low-energy electron diffraction (LEED) patterns can be chosen as calibration points, but it is not certain that the calibration is good for submonolayer coverages unless the adsorption kinetic is known [2]. We have found that thermal desorption spectroscopy (TDS) can be conveniently used

for calibration. It measures the number of molecules desorbed from a surface per unit time [3]. Since the time-integrated TDS signal yields the total number of molecules desorbed from the surface, the number of molecules left on the surface can be deduced if the initial surface coverage is given. In this paper, we report our recent endeavor to demonstrate experimentally that such a calibration procedure is indeed valid. In our work, we chose adsorbate/substrate systems whose adsorption kinetics, and hence the surface coverages, could be determined directly from SHG. The surface coverages deduced from SHG could then be compared with those obtained from the TDS measurements. We remember that although SHG and TDS can both yield information on surface coverages, the former measures directly the amount of adsorbates on a substrate while the latter measures the amount of adsorbates leaving the substrate. SHG has the advantage of having a much faster time response and can be conveniently used to study dynamics of molecular adsorption and desorption at a surface [4].

The experiment was carried out in an UHV chamber which was equipped with the usual surface cleaning and analyzing tools. The operating pressure of the chamber was around 4×10^{-10} Torr. Adsorption and desorption of CO on Cu(100) and Ni(111) were studied. The Cu sample was cleaned by cycles of Ar^+ sputtering, heating in 5×10^{-5} Torr of O_2 followed by heating in 1×10^{-6} Torr of H_2 , and annealing at 250°C . The Ni sample was cleaned by cycles of Ar^+ sputtering and annealing at 680°C . Surface cleanliness of the samples was verified with Auger electron spectroscopy and LEED. Flash heating was used to ensure surface cleanliness before data taking. The CO dosage to the samples was monitored by a UTI quadrupole mass spectrometer. The same equipment was used to obtain thermal desorption spectra, which could be taken simultaneously with the SHG measurement. The latter was carried out with a pulsed Nd:YAG laser beam at $1.06 \mu\text{m}$ and $0.532 \mu\text{m}$ incident at 45° onto the samples. To avoid surface damage or laser desorption of CO, the laser power was limited to 6 mJ on Ni(111) over a 6 mm^2 spot and 1.4 mJ on Cu(100) over a 37 mm^2 spot. The SH signal was detected by a photomultiplier tube and processed by a gated electronic system.

We first consider CO adsorption on Cu(100). The sample was kept at $T = 140 \text{ K}$. For $T \geq 140 \text{ K}$, it is known that CO adsorbs on Cu(100) only at the top sites [5]. One would then expect that the adsorption kinetics might obey the Langmuir model as in the case of CO on Rh(111) [2]. That this was indeed the case was indicated by the SHG results from CO on Cu(100). The SH signal S versus CO surface coverage θ should take the form

$$S = |A + B\theta/\theta_s|^2, \quad (1)$$

where A and B are constants, θ is the CO surface coverage relative to a monolayer of Cu(100), and $\theta_s = 0.5$ is the saturation coverage denoted by the uncompressed $c(2 \times 2)$ LEED pattern. The A term comes from the bare metal

surface contribution, while the B term arises from the surface coverage. According to the Langmuir kinetic model, the surface coverage θ increases with exposure following the equation [6]

$$\theta = \theta_s \left[1 - \exp\left(-\frac{\alpha\Gamma}{N_s\theta_s p} D\right) \right]. \quad (2)$$

Here, $D = pt$ is the exposure (in Langmuir units), p is the gas pressure, N_s is the surface atomic density of the substrate, Γ is the rate of molecules impinging on the surface, and α is the initial sticking probability. Insertion of eq. (2) into eq. (1) gives S as a function of D , which can be used to compare with the experimental results. This is depicted in fig. 1 for CO on Cu(100). It is seen that by normalizing the signal to that at $\theta = \theta_s$, and using B/A and $(\alpha\Gamma/N_s\theta_s p)$ as adjustable parameters, the theoretical curve describes the experimental data very well, indicating that CO adsorption on Cu(100) at ~ 140 K indeed follows the Langmuir kinetics. Other researchers have reported observation of different adsorption kinetics for the same system [5]; in their case, however, the system was at a much lower temperature and the adsorption of CO went through two different stages. From theoretical fit with

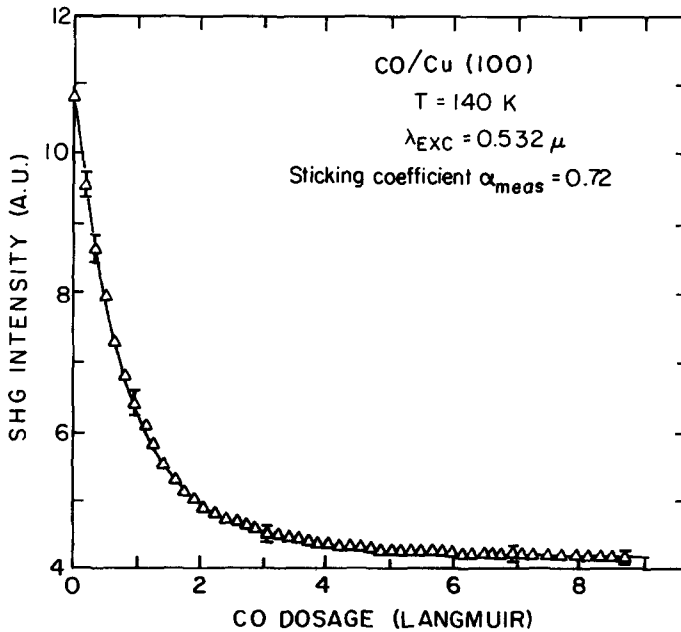


Fig. 1. Second harmonic generation as a function of surface coverage of CO on Cu(100) at 140 K. The solid theoretical curve derived from the Langmuir kinetic model is used to fit the experimental data points (Δ).

the experiment, we obtain $B/A = -0.37$ and $\alpha\Gamma/N_s\theta_s p = 0.48/\text{L}$. The latter allows us to deduce the initial sticking probability $\alpha \sim 0.7$ knowing that in our experiment, $N_s = 1.53 \times 10^{15}/\text{cm}^2$, $\theta_s = 0.5$ and $\Gamma/p = (2\pi M_{\text{CO}} k_B T)^{-1/2} = 4.2 \times 10^{17}$.

In the subsequent thermal desorption experiment, we raised the temperature of Cu(100) covered with a saturated monolayer of CO uniformly from 140 to 230 K and monitored simultaneously SHG and TDS. In this temperature range, eq. (1) still holds and the constant $B/A = -0.37$ is expected to be insensitive to the temperature variation. Using eq. (1), we can then deduce θ/θ_s from the measured SH signal for CO on Cu during the desorption process. The same information can be obtained from TDS. Since the TDS signal is proportional to $\partial\theta/\partial T$, a normalized integration of the thermal desorption spectrum gives

$$\int_{T_i}^T \frac{\partial\theta}{\partial T} dT \bigg/ \int_{T_i}^{T_f} \frac{\partial\theta}{\partial T} dT = 1 - \theta(T)/\theta_s. \quad (3)$$

The resulting θ/θ_s can be directly compared with that deduced from SHG. Alternatively, we can insert the value of $\theta(T)/\theta_s$ obtained from TDS into eq.

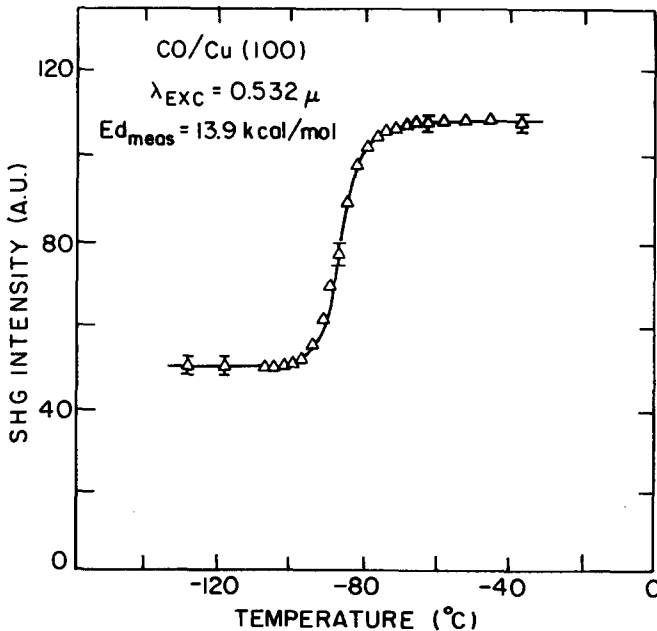


Fig. 2. Second harmonic generation from CO on Cu(100) as a function of desorbing temperature. The solid curve is calculated from thermal desorption spectroscopy data, and the triangular points are obtained from direct measurements.

(1), calculate the SH signal $S(T)$, and compare it with the measured $S(T)$. The latter was actually the procedure we adopted in comparing SHG and TDS. The results are shown in fig. 2. The SH signal versus T calculated from the TDS data are in very good agreement with the directly measured SH signal. This then proves our conviction that one can use TDS to calibrate SHG as a tool for monitoring surface coverage.

As another example, we consider CO on Ni(111). At $T \geq 300$ K, CO adsorbs on Ni(111) only at the two-fold bridge sites [7]. We again anticipated that the adsorption would follow the Langmuir kinetic model. Our SHG result presented in fig. 3 shows that this is indeed the case. The experimental data on SHG from CO/Ni(111) as a function of CO exposure at 300 K can be well described by eq. (1) together with eq. (2). The fit leads to the determination of the following parameters: $B/A = 0.9 \times \exp(i165^\circ)$ and $(\alpha\Gamma/N_s\theta_s p) = 0.37/L$. Knowing that $N_s = 1.87 \times 10^{15}/\text{cm}^2$, $\theta_s = 0.5$ [as calibrated by the $c(4 \times 2)$ LEED pattern [7]], and $\Gamma/p = (2\pi M_{\text{CO}} k_B T)^{-1/2} = 2.87 \times 10^{17}$, we find the initial sticking probability to be $\alpha \sim 1$, which agrees with the value obtained from the work-function study [7,8]. The Langmuir kinetics leads to a sticking probability decreasing linearly with the CO coverage. This is different from that deduced from the work-function study [8]. The reason of this discrepancy

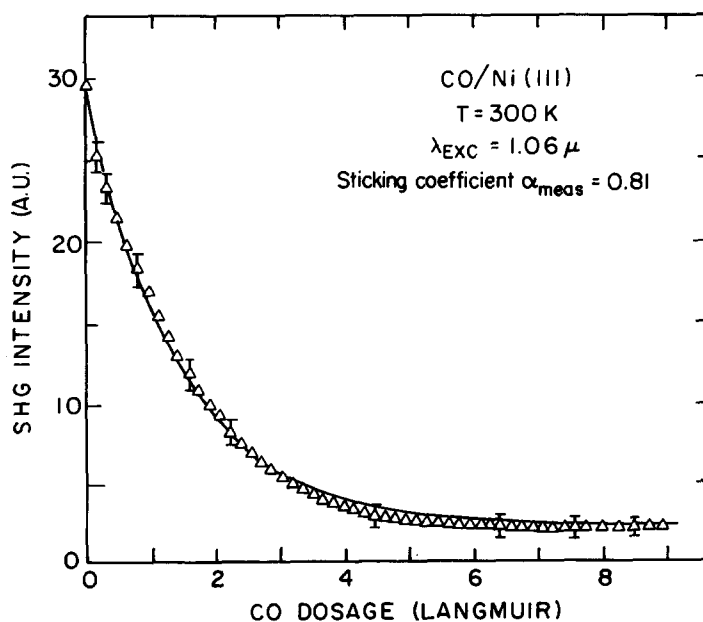


Fig. 3. Second harmonic signal as a function of surface coverage of CO on Ni(111) at 300 K. The solid theoretical curve derived from the Langmuir kinetic model is used to fit the experimental data points (Δ).

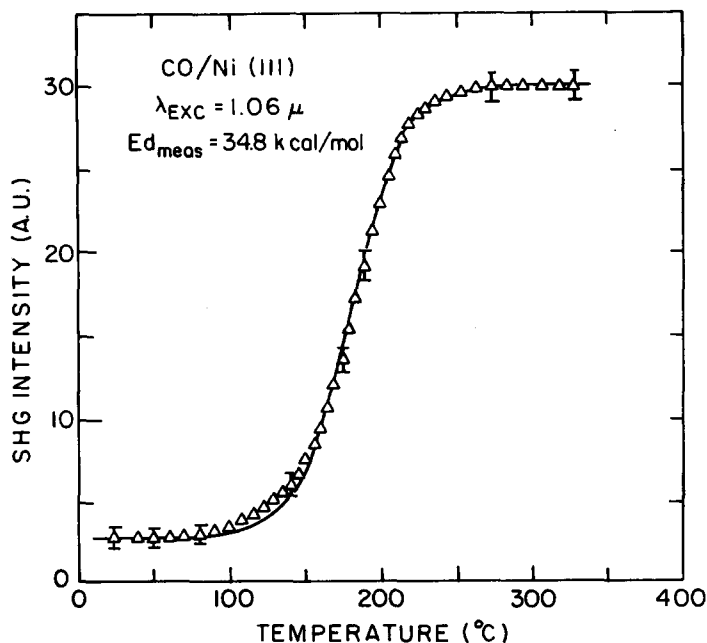


Fig. 4. Second harmonic signal from CO on Ni(111) as a function of desorbing temperature. The solid curve is calculated from thermal desorption spectroscopy data, and the triangular points are obtained from direct measurements.

is not clear, but we note that our SHG measurement is a more direct probe of CO adsorption as a function of time than the work-function study. After θ approaches θ_s , the sample was heated up uniformly in time, and the thermal desorption was simultaneously monitored by SHG and TDS. Again, $\theta(T)/\theta_s$ can be deduced from an integration of the TD spectrum; its insertion in eq. (1) with B/A already determined allows us to predict the SH signal which can be compared directly with the measured SH signal. This is shown in fig. 4. The agreement between the predicted and the measured SH signals is again remarkably good.

Thus, from the above two demonstrated cases, we have established the correlation between TDS and SHG. This means that through calibration against TDS, it is now possible to use SHG to measure quantitatively the surface coverage of an adsorbed species. The conclusion here is true in general, irrespective of the detailed adsorption kinetics. This is most interesting because otherwise SHG as a technique for monitoring surface coverage is limited to cases where the adsorption kinetics is known. Through calibration against TDS, the technique is now applicable to all cases.

In comparison with TDS (and other surface tools) for monitoring surface coverage, SHG has the following obvious advantages. It is sensitive, non-detri-

mental, and capable of remote sensing and in situ measurements over a small restricted area on the surface. Contrary to TDS, it measures directly the surface coverage, and is applicable to both static and dynamic cases. Unlike TDS, SHG can be used to monitor surface coverage when adsorption and desorption processes are simultaneously present. The technique has an essentially instantaneous response, and will be most useful in studies of dynamics of molecular adsorption and desorption.

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